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Art. XX.—*High Frequency Spectra—K Series of Platinum.*

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(With Text Figs. 1a, 1b, and 2.)

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Introduction.

The purpose of this paper is to describe a precise method of measuring the wave lengths of the high frequency spectrum of platinum.

The method employed is one in which a rotating crystal spectrometer is used, and the platinum lines, together with those of tungsten, are recorded on the same film. The wave lengths of the platinum lines are deduced by inter- and extra-polation from the tungsten lines, the wave lengths of which are known with great accuracy, having been measured recently with great precision by Siegbahn,[1] and by Duane and Stenstrom.[2]

The investigation of the K lines of platinum, in common with those of other heavy elements, is beset with certain difficulties, which have prevented the spectra of these elements being determined.

In order to excite efficiently the K spectrum of an element of high atomic number, it is necessary to use the substance as target in an X-ray tube. A very high potential difference must then be applied to the tube, since a minimum pressure of 78,000. volt is required to obtain the K series of platinum. Under such high pressures there is always the risk that the tube will fail. Again, a very high vacuum must be present in the tube. In the case of a gas-filled tube this became a source of considerable difficulty, for, even when the requisite vacuum is obtained, the tube becomes very uncertain in operation, and, under the very best conditions, only a small current can be passed through the tube. In consequence, the X-rays produced possess

1. Phil. Mag. XXXVIII., Nov., 1919.
2. Proc. Nat. Acad. Sci., VI., 1920, p. 477.

but a small amount of energy, and have very little photographic effect. It is thus essential to have long exposures.

The photography of the lines is complicated still further by the photographic fog produced by the rays scattered by various parts of the apparatus (slits, crystal, etc.). Since the lines occur on the film very close to where the direct rays fall, the scattered rays are most intense just at the region where the lines are to be observed.

The one heavy element, the high frequency spectrum of which has been carefully investigated, is tungsten. Since this element has been used as the material of the target in the Coolidge type of tube, it is a comparatively easy matter to excite its K series spectrum. As there was no Coolidge type of tube with a platinum target available for this research, a gas-filled tube, made by Gundelach, was used.

The K series of platinum has been measured once previously —by Lilienfeld and Seeman,[3] who employed a Lilienfeld tube with a target of platinum-iridium. The values obtained by these authors are given in Table II.

The Spectrometer.

The whole of X-ray spectroscopy is based on the fact that a crystal acts as a space grating to X-rays. W. L. Bragg[4] showed that if a parallel beam of X-rays of wave-length λ was directed on a crystal face at an angle θ so that $\lambda = 2d \sin \theta$, there would be an interference maximum at an angle θ, and other maxima at values of θ given by $n\lambda = 2d \sin \theta$; n is here an integer and d is the lattice constant of the crystal, i.e., the distance between successive planes of atoms, parallel to the reflecting face. If, then, it is desired to resolve a beam of X-rays into its component parts, it is necessary that the crystal should be placed at different angles with respect to the incident beam. This is done most efficiently by rotating the crystal slowly and uniformly.

Further, W. H. Bragg[5] established that if a diverging beam of X-rays issued from a narrow slit S_1 (fig. 1(*b*)), and fell on a crystal face which was rotating about a point O (axis of rotation), and if a photographic film was placed round the circle

3. Phy. Zeit., XIX., 1918, p. 269.
4. X-Rays and Crystal Structure, p. 16.
5. X-Rays and Crystal Structure, p. 31.

FF′, which has O as centre, and OS_1 as radius, all the X-rays of a certain wave length λ would be reflected to a particular vertical line on the film. If there is present in the incident beam X-rays of a definite wave length, carrying more energy than those of adjacent longer and shorter wave legths, then its presence will be shown by a line on the film.

An additional advantage of a rotating crystal is that it gives much sharper lines than a stationary one, since the effect on the lines of surface defects of the crystal is thus considerably lessened.

No spectrometer being available, a Dancer theodolite was modified to have the movements of a spectrometer, and to fulfil the requirements of the focussing condition. It may be mentioned that a theodolite can be adapted to form a spectrometer, which is both accurate and convenient.

The circle carrying the scale was fixed by shrinking a brass ring on to its under surface at AA′ (fig. 1a). This ring was supported by a tripod mounted on the ring BB′, through which passed three levelling screws bearing on a stone table. The crystal holder was mounted on the vernier circle at D. The film holder was carried by an arm which screwed into the theodolite at E. Both crystal holder and film holder turned on conical bearings. The slits S_1 and S_2 were supported by a brass tube which screwed into the ring BB′.

The *crystal* was a large calcite one. The reflecting face (5.cm. x 2.cm.) was a ground cleavage one. As W. L. Bragg, James and Bosanquet[6] have shown, ground faces are more efficient reflectors than natural cleavage faces.

The *crystal holder* was so designed that the reflecting face of the crystal could be made vertical, and could be brought into the axis of rotation of the spectrometer.

The *film holder* was cut from a brass ring, the inside edge of which was accurately turned, its radius being $10.001 \pm .001$ cm. The film, in its paper casette, was tightly pressed against this by means of two curved strips of red fibre and clamping screws.

Slits.—The slit S_1, the tube slit, was made of an alloy of lead and antimony (75 per cent. lead), such an alloy being more durable than pure lead. The inside faces of this slit were carefully ground, and the slit width could be adjusted by a screw to 0.005. mm. The slit S_2 was made of lead, and was carried by the

6. Phil. Mag., XLI., 1921, p. 309.

same holder as S_1. This holder was constructed to allow the following adjustments: (a) It could be moved towards the axis of rotation of the spectrometer; (b) S_1 could be made vertical;

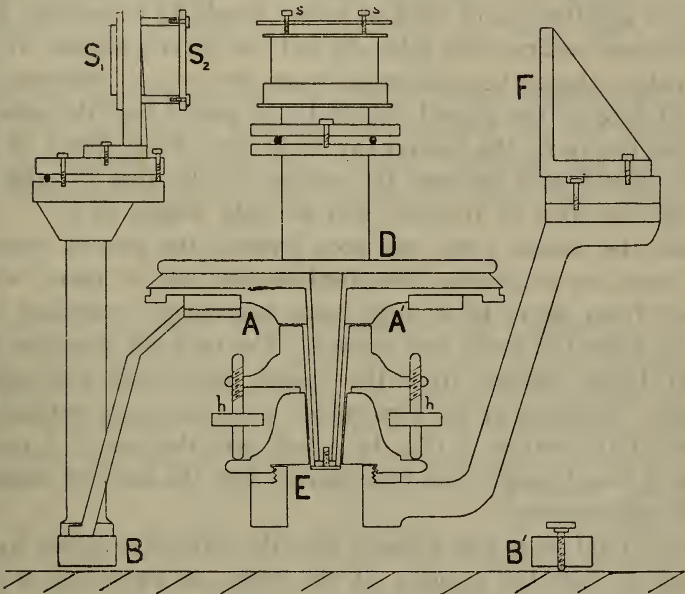

FIGURE 1A

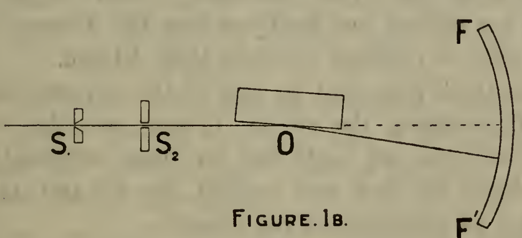

FIGURE. 1B.

DIAGRAM OF THE SPECTROMETER

(c) the line joining the centres of the slits could be made to pass through the axis of rotation.

Rotation Apparatus.—The vernier circle was rotated by means of a tangent screw. By means of a reduction gear, this was turned at 1/10,000th of the speed of a small motor. In the experiments, the rate of rotation of the crystal was about 2° per hour.

Adjustments.

The following are the essential requirements of a spectrometer of this type: The tube slit, the axis of rotation of the spectrometer and the axis of the film holder should all be parallel, and, in this case, vertical; the tube slit and the curved portion of the film holder should be equidistant from the axis of rotation; the ground face of the crystal should be so placed that the axis of rotation lies in it; the central ray from the "focal spot" of the target should pass through the centres of the slits S_1 and S_2, through the axis of rotation, and at right angles to it.

After the vernier circle had been levelled, the axis of rotation was found by so placing a vertical needle that its point, when viewed from above by a long focus microscope, remained stationary when the circle was rotated. The tube slit was then adjusted 10.cm. distant from the needle point, and was placed vertical. The axis of the film holder was next made vertical by means of the screws *h* (fig. 1a) ; and with the use of a centre tester, it was brought into coincidence with the axis of rotation of the spectrometer.

The crystal face was brought into the axis of rotation by so placing it, that the position of the edge, as viewed in a low power miscroscope, with its axis vertical, was in the same position both before and after the crystal had been rotated through 180°. The adjustment was carried out finally so that the distance of the face from the axis of rotation was less than .01.mm.

An optical method was used to test if the crystal face was vertical. By illuminating the slit S_1 it was possible to view, in a telescope, both the slit itself and its image reflected in the crystal face. When the face was vertical, the slit and its image were parallel for all positions of the crystal.

The slit S_1 was then so turned, and the crystal face was so placed that the light from the slit passed along the crystal face both before and after the crystal was rotated through 180°. This adjustment was carried out by means of a telescope, and it ensured that the ray from the centre of S_1 passed through the axis of rotation. The sides of the slit S_2 were then placed symmetrically with respect to those of S_1. In the experiments the widths of the slits were: S_1, 0.08. to 0.1.mm.; S_2, 0.6.mm.

The focal spots on the targets of both tubes were clearly marked. The focal spot in the case of the Coolidge tube was illuminated by lighting the filament, but for the Gundelach tube, light from a lamp was focussed on the target. The focal spot was viewed through a horizontal telescope, placed at the same height above the table as the centre of the crystal face, and the necessary adjustments for the central ray were easily carried out.

In the experiments described below it was necessary to adjust the focal spot of the Coolidge tube when it was not possible to use a telescope. In this case a mirror was used, and the images of the focus, slit and crystal face were viewed from above.

Experiment.

Tube.—The target of the Gundelach tube consisted of a platinum button attached to a stout copper rod, on the external end of which was a brass radiator. The potential difference applied to the tube was produced by a Snook-Victor high tension rectifier.

At the beginning of the research, the tube was too soft to excite the K series of platinum. The maximum pressure that could be applied to the tube was 60,000.volt. If the switches on the high tension rectifier were turned to increase the pressure, the only result was an increase in the current passing through the tube. It was found, however, that by keeping the current low —less than 0.5.m.a.—that the tube gradually hardened. After a fortnight's running, for several hours a day, a pressure of 85,000. volt could be applied to the tube. It was found difficult to maintain this potential difference, because fluctuations in the current became very big, and, with the increase in current there was the consequent drop in pressure.

After a considerable amount of experiment the following procedure was adopted. The tube was allowed to harden, so that there was practically no current, when a pressure of 95,000. volt was applied. Then, to begin an experiment, the tube was slightly softened, so that a current of 0.6.m.a. was obtained at 85,000.volt. If the current became less, the pressure was raised, and usually this gave an increase in current. The usual experience was, however, that the current, with the attendant fluctuations, increased after about 15.min., so that the corresponding falls in pressure were less than 80,000 volt. This was probably due to the target, as it became heated, giving off occluded gas. The pressure was then cut off from the tube for between

5. and 10 min., and, at the end of this time, the tube would be again in a condition suitable for use. To obtain lines sufficiently intense to measure, an exposure of 10,800 milliampere sec. was necessary. Since the average current through the tube was between .7. and .8.m.a., such an exposure required an experiment of at least six hours. The greater intensity of the radiation from a Coolidge tube was shown by the fact that more intense lines were obtainable from it in 5 min.

The *film used* was Eastman Dulpli-tized (photographic emulsion on both sides) which was placed between two Patterson intensifying screens. It has been stated that sharply defined lines cannot be obtained when intensifying screens are used. However, quite satisfactory lines were obtained, since under these conditions the α doublet of tungsten was resolved with a slit width of 0.12.mm. One great advantage of the doubly-coated film is its rigidity—there is no tendency to buckle during drying. Had intensifying screens not been used, the exposures would have been so long as to be practically impossible.

Protection from Scattered Radiation.—A sheet of aluminium 0.6.mm. thick was placed in front of the film to absorb the soft scattered radiation. In addition the rays reflected from the crystal were made to pass along a channel the sides of which were constructed of lead 3.mm. thick. This channel converged on all sides towards the crystal where its opening was a rectangle 2.cm. x 6.mm. This was large enough to allow both the direct rays and the lines to fall on the film.

Reference Lines.—The Pt. lines were photographed on the top half of each film, the lower part being covered with a lead screen. The Coolidge tube was then substituted for the Gundelach, and the W lines were photographed on the lower portion of the film. Since the film was held by the red fibre strips (vide page 198), there was no opportunity for it to slip during an experiment. The lines appeared as shown in figure 2. It will be seen that the α doublet of platinum falls between the α and β lines of tungsten. (The thickness of lines in the figure indicates relative intensities.)

Measurement of Lines.—The film was projected by a lantern, and a magnification up to 10 was obtained. The lines on each film were measured at three different magnifications, and the mean of the values so obtained was taken as the wave lengths of the lines given by the film.

A dividing engine, with a very accurate screw, was adapted for measuring the distance between the lines. A vertical board was carried by the moving platform of this engine. Two vertical lines 1.5.mm. apart were drawn on this board, and each line on

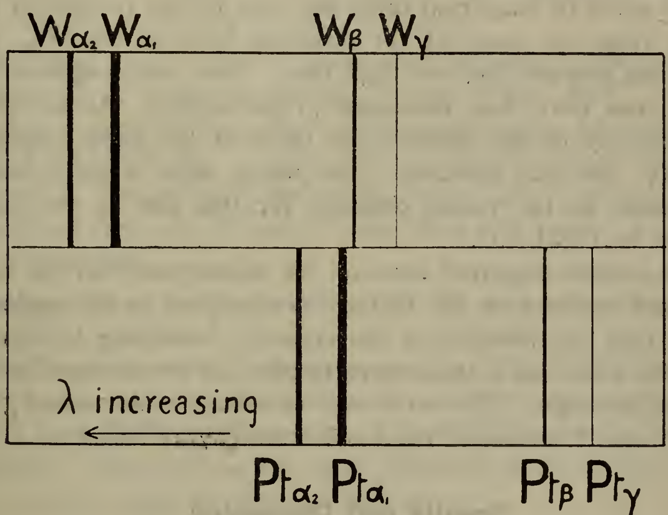

FIGURE 2.

the film was brought in turn exactly between these lines, and the reading of the engine noted. Table I. shows a set of such readings.

TABLE I. (Distances in mm.).

—	W.α_2.	W.α_1.	Pt.α_2.	Pt.α_1.	W.β.	W.γ.	Pt.β.	Pt.γ.
	0	1·13	5·87	7·10	7·25	8·51	12·46	13·66
	0	1·18	5·84	7·14	7·30	8·48	12·23	13·46
	0	1·15	5·90	7·18	7·29	8·50	12·38	13·47
	0	1·14	5·90	7·10	7·29	8·42	12·36	13·41
	0	1·15	5·88	7·22	7·33	8·41	12·29	13·50
Mean -	0	1·15	5·878	7·144	7·296	8·472	12·34	13·50

It will be seen that, for the fainter lines, e.g., the β and γ lines of Pt., there is much greater variation in setting than for the more intense lines. To evaluate the wave lengths the mean of

Siegbahn's and Duane and Stenstrom's values were assumed. These are as follow:—

$$\lambda \textit{ for } W\alpha_2 = \cdot 21347 \times 10^{-8}\text{cm}$$
$$W\alpha_1 = \cdot 20873 \quad ,, \quad ,,$$
$$W\beta = \cdot 18428 \quad ,, \quad ,,$$

The value in Angstrom units per mm. of the projection was found from the mean of the distances between the $W\alpha_2$ and $W\beta$ lines, and the $W\alpha_1$ and $W\beta$ lines. The wave lengths of the other lines were then calculated proportionally. As a test of the accuracy of the method, the value of the wave length of the $W\gamma$ line was obtained. The mean value is given below. The mean of the values obtained for this line by the above authors is .17921.A.U.

The method employed rests on the assumption that the wave lengths of the lines on the film are proportional to the angles at which they are reflected at the crystal. According to Bragg's formula, $\lambda = 2d \sin \theta$, these wave lengths are proportional to the sine of the angle. No error was introduced in the values given below since θ for $K\alpha_2 = 2°$(*q.p.*) and θ for Pt.$\gamma = 1°30'$(*q.p.*)

Results and Discussion.

In Table II. are given the values obtained. The wave lengths were calculated to five decimal places, and the final values are given to four places, with the probable error.

Table II. (λ in Angstrom Units).
Wave Lengths of K Series of Platinum.

Film No.	Pt.α_2.	Pt.α_1.	Pt.β.	Pt.γ.	W.γ.
P.14	·18939	·18496	·16455	·15955	·17952
P.15	·18926	·18536	·16427	·15968	·17905
P.16	·18998	·18502	·16429	·15942	·17973
Mean - -	·18954	18511	·16437	·15955	·17943
Final - -	·1895±2	·1851±1	·1644±2	·1596±2	·1794±2
Lilienfeld and Seeman	·1907	·1853	·1642	·1593	—

In the last line of the table the values obtained by Lilienfeld and Seeman are inserted for comparison. The agreement is good except for the Pt.α_2 line. The apparent discrepancy can be explained by the fact that these authors were unable to distinguish between the Pt.α_2 line and the Ir.α_1 line. The writer has found that if the K spectra of Pt. and W are photographed on the same portion of a film, it is impossible to recognise as separate lines, the Wβ (λ=·1843) and Pt.α_1(λ=·1851)

Theory of Lines.—The K series of an element is excited when an electron is ejected from the K ring of the atom. If this electron is replaced from the L ring of the atom, the energy so freed gives rise to the α_1 line. If it is replaced from an electron from the L′ ring (an elliptical orbit), the α_2 line is excited. Replacements from the M and N rings give rise to the β and γ lines respectively.

Moseley's formula, $\frac{v}{R} = (N-1)^2(1/1^2 - 1/2^2)$, for the wave number v of the Kα_1 line, which accurately represents the observed values for low values of N, fails for elements of higher-atomic number. (R is here Rydberg's constant, N the atomic number of the element.) The value of the wave length of the Pt.α_1 line from this formula would be .2049 x 10^{-8} cm.

Sommerfeld has developed a formula for the wave number $v(=1/\lambda)$, by considering the effective nuclear charge for the K and L rings as (N– 1.6) and (N–3.5) resp. and by taking into account the relative masses of the electrons in consequence of their velocity. The formula is:—

$$v/R = \frac{2}{\alpha^2}\left(\sqrt{1 - \frac{\alpha^2}{4}(N-3\cdot5)^2} - \sqrt{1 - \alpha^2(N-1\cdot6)^2}\right)$$

where $\alpha = \frac{2\pi e^2}{ch}$ e, c, h being the charge on the electron, the velocity of light and Planck's constant respectively. Hence $\alpha^2 = 5.3088 \times 10^{-5}$.

This formula gives λ for Kα_1 of Pt.=·1837 × $10.^{-8}$ cm.

A formula due to Kroo and Sommerfeld fits the observed value more accurately still. In this, before the passage of the atom, which gives rise to the Kα_1 line, the K ring is considered as a 1 quantum ring with 2 electrons, the L ring as a 2 quanta ring with 9 electrons. After the passage of the electron, the K ring is a 1 quantum ring with 3 electrons, and the L ring as a 2 quanta ring with 8 electrons. By calculating the energy difference between the two configurations, the following formula is obtained:—

$$\frac{v}{R}=\frac{2(k-1)}{\alpha^2}\sqrt{1-\alpha^2F_1}+\frac{2(l+1)}{\alpha^2}\sqrt{1-\alpha^2F_2}-\frac{2k}{\alpha^2}\sqrt{1-\alpha^2F_3}$$
$$-\frac{2l}{\alpha^2}\sqrt{1-\alpha^2F_4}$$

where $k=3$, $l=8$, $F_1=(N-S_{k-1})^2$, $F_2=\frac{1}{4}(N-k+1-S_{l+1})^2$, $F_3=(N-S_k)^2$, $F_4=\frac{1}{4}(N-k-S_l)^2$

and the S terms are obtained from

$$S_p=\frac{1}{4}\sum_{1}^{i=p-1}\frac{1}{\sin i\frac{\pi}{p}}$$

For Pt. this gives the values of $\lambda.K\alpha_1$ as $\cdot 1841\times 10^{-8}$ cm. The agreement with the observed value is remarkable, as the formula is a rational relation. This lends additional support to the Bohr-Sommerfeld theory of the atom.

Sommerfeld has also obtained the following formula for the difference in wave number Δv for the lines of the $K\alpha$ doublet:—

$$\frac{\Delta v}{(N-3\cdot5)^4}=\Delta v_H\left[1+\frac{5\alpha^2}{2}.\frac{(N-3\cdot5)^2}{2^2}+\frac{53\alpha^4}{8}.\frac{(N-3\cdot5)^4}{2^4}\;.\;.\;.\;.\;.\right]$$

where Δv_H=frequency difference for hydrogen$=\frac{R\alpha^2}{2^4}$.

From the results of the experiment, given in Table II., $\Delta v\times 10^8=\cdot126\pm\cdot008$, while the above formula gives $\Delta v\times 10^8=\cdot135\pm\cdot002$.

It will be seen that the agreement is again fairly good.

In conclusion, the author wishes to express his indebtedness to Prof. T. H. Laby, M.A., Sc.D., F. Inst. P., for his invaluable guidance and advice throughout the whole of the research, and in the writing of this paper.

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